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ICP-OES Analysis of the Chemical Composition of Hypergolic Mixtures

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Abstract

Hypergolic mixtures involve a chemical reaction between an oxidant and a fuel source. These reactions are self-igniting and can be performed using common household materials. The ease of access to the reactants, and delayed ignition have increased the occurrence of hypergolic mixtures in arson-related crimes and incendiary devices. Currently, few chemical signatures exist to link hypergolic residues to a perpetrator. This makes it difficult to obtain forensically relevant information from evidence during an investigation. A hypergolic reaction of interest to forensic laboratories involves combustion between a glycol-based fuel source and potassium permanganate. Past studies have determined that one can distinguish between the oxidant and fuel used in a reaction based upon the composition of the residues or the extent of the reaction. The aim of this study is to determine the forensic signatures of reactions involving varying glycol fuel sources: brake fluid and antifreeze. Elemental profiles of residues were created using Inductively Coupled Plasma-Optical Emission Spectroscopy. Results showed that the metal composition of a residue sample was valuable in distinguishing between possible glycol fuel sources in hypergolic reactions, and that the ratio of oxidant to fuel source had minimal effect on the metal composition.

Introduction

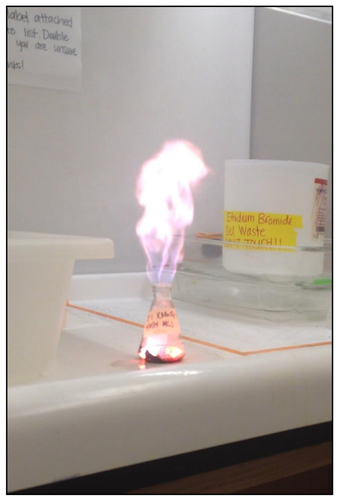
Homemade incendiary devices are a major concern due to the ease of which materials can be obtained. One type of hypergolic reaction of interest to forensic laboratories involves combustion between a glycol-based fuel source and potassium permanganate.[1] This reaction is characterized by delayed ignition, which is why these reactions are commonly used in criminal activities. Currently, few chemical signatures exist to link hypergolic residues to a perpetrator.[2] This makes it difficult to obtain forensically relevant information from evidence during an investigation. Past studies have determined that one can distinguish between the oxidant and fuel used in a reaction based upon the composition of the residues or the extent of the reaction. For example, observation of reactions revealed that potassium permanganate ($KMnO_4$) is an oxidant that generally results in more violent incendiary devices than those where trichloroisocyanuric acid (TCCA) chlorine sources are employed.

Through more research, individual characteristics of these reactions can be determined. Trace element analysis will allow for the determination of chemical variation between the sources used to carry out reactions. Therefore, we have designed a study to investigate the differences in residues obtained from hypergolic reactions involving varying glycol fuel sources.

Methods

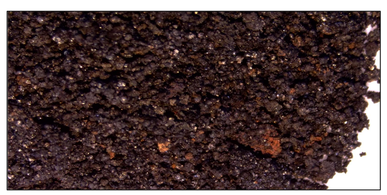
Creation of Residues:

Potassium permanganate and sources of glycol fuel were purchased from scientific supply companies and local retailers. Residue samples were prepared by adding $KMnO_4$ to a glycol fuel source of brake fluid or antifreeze. For each trial, a mass of 2g or 3g $KMnO_4$ was measured and transferred to a 125 mL Erlenmeyer flask-depending on whether the reaction was 2:1 or 3:1. A 1 mL volume of the glycol fuel was dispensed and pipetted over the oxidant. The process was repeated so that there were at least two replicates of each oxidant-glycol fuel ratio for each glycol fuel



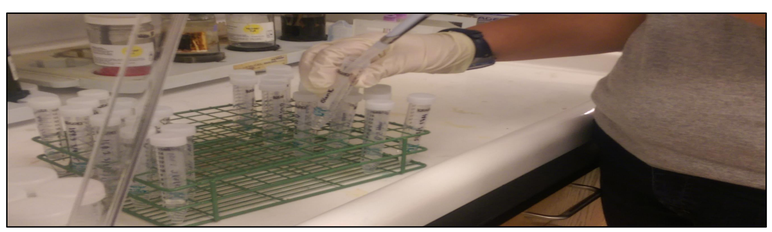
Acid Digestion and Extraction:

A mass of ~0.5 g of each dry, collected residue was transferred to a 50 mL trace metal free tube, and digested using 10 mL of 2% nitric acid. The conical tubes were vortexed and allowed to sit for thirty minutes at room temperature. The contents of each tube was spun down in a centrifuge at 3095 x g for 10 minutes, after which a minimum of 6 mL of the supernatant was transferred into a clean 15 mL metal free conical tube. This was done until there were no particles remaining in the extract.



Analysis via ICP-OES

IV-Stock-8 standards ranging from 0.005-100 ppm were prepared using 2% nitric acid. Trace metal analysis was performed on the standards and extraction samples through inductively coupled plasma-optical emission spectroscopy. A spectrum of intensity versus concentration was obtained for data analysis and elemental concentration was calculated.



Results

	B	Mn	Pb	Te	Co	Fe
2:1 Brake Fluid	16.87	17.01	ND	ND	ND	ND
2:1 Brake Fluid	10.43	15.56	ND	ND	ND	ND
3:1 Brake Fluid	6.80	14.00	ND	ND	ND	ND
3:1 Brake Fluid	6.34	36.98	ND	ND	ND	ND
2:1 Antifreeze	4.89	90.57	0.10	0.04	0.02	0.04
2:1 Antifreeze	4.28	93.09	0.11	0.05	0.02	0.01
3:1 Antifreeze	3.53	90.88	0.10	0.01	0.02	ND
3:1 Antifreeze	3.11	81.43	0.04	0.01	ND	0.09

Table 1. Concentration of metals in residue acid digestions. ND= Not detected. Concentrations measured in ppm.

Conclusion

In this study, hypergolic reactions were conducted to determine the effects of the ratio of the oxidant-fuel components and different glycol fuel sources on residues. The metal composition of a residue sample was determined to be valuable in distinguishing between possible glycol fuel sources in hypergolic reactions and the ratio was shown to have little effect on the metal composition of the residue.

Works Cited

[1] Beveridge, A. *Forensic Investigation of Explosions*, 2nd ed. CRC Press: Northwest, Washington, DC. , 2012. pp 84, 487.

[2] Zimmerman, A. Clinical Profiling of Trichloroisocyanuric Acid (TCCA) Based Explosives for the Forensic Attribution of Precursor Materials. In AAFS 2014, Seattle, WA, Feb 21; VCU Department of Forensic Science; A125.

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